# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-081131

(43)Date of publication of application : 27.03.2001

(51)Int.Cl. C08F 8/14
C08F 2/50
C08F 8/00
C08F 8/32
C08F 14/22
C08F290/04
C08G 18/62

(21)Application number : 11-264477

(22)Date of filing : 17.09.1999

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## (54) FLUOROOLIGOMER CONTAINING FUNCTIONAL GROUPS AT BOTH TERMINALS OF MAIN CHAIN, ITS PRODUCTION AND CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a curable composition which can produce a cured product having excellent toughness, excellent elasticity, excellent elasticity, and the like at a high curing rate by allowing a curable composition to contain a fluorooligorrter containing functional groups at both the terminals of the main chain.

SOLUTION: The fluorooligomer containing ester groups at both the terminals of the main chain, the fluorooligomer containing, unsaturated groups at both the terminals of the main chain, or the fluorooligomer containing alcoholic hydroxyl groups at both the terminals of the main chain is a fluorooligomer which has a number-average mol.wt. of 1,000 to 10,000 and has ester groups, unsaturated groups or alcoholic hydroxyl groups at both the terminals of the main chain of the fluorooligomer. The method for producing the fluorooligomer having the unsaturated groups or the alcoholic hydroxyl groups at both the terminals of the main chain comprises reacting the fluorooligomer having the ester groups at both the ends of the main chain with an unsaturated group-containing amine or an alcoholic hydroxyl group-containing amine at ≤60°C. The curable composition comprises the fluorooligomer containing the unsaturated groups at both the terminals of the main chain, (meth)acrylic monomer, and a photopolymerization initiator or a radical-generating agent. The curable composition further comprises the fluorooligomer containing the alcoholic hydroxyl groups at both the terminals of the main chain and a polyisocyanate compound.

* NOTICES *



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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the fluoride oligomer which has an alcoholic hydroxyl group in the both ends of the fluoride oligomer which has an ester group in the both ends of a main chain, the fluoride oligomer which has an unsaturation group in the both ends of a main chain, and a main chain. It is related with the manufacturing method of these fluoride oligomer. Furthermore, It is related with the hardenability constituent which becomes both ends of the hardenability constituent which becomes both ends of a main chain from fluoride oligomer, acrylic monomer (meta) and photopolymerization initiator which have an unsaturation group, or a radical generator, and a main chain from the fluoride oligomer which has an alcoholic hydroxyl group, and a polyisocyanate compound.
[0002]
[Description of the Prior Art] The fluoride oligomer which has a carboxyl group in the both ends of a main chain is a compound expected as a compound useful as raw materials, such as chain elongation agents, such as an epoxy resin and isocyanate resin, or solvent resistance sealant, adhesives, and a paint. Conventionally the fluorine-containing oligomer which has a carboxyl group in both ends, For example, although a fluoridation vinylidene-hexafluoro propene copolymer is formed into dehydrogen fluoride on the US,3,291,761,B Descriptions, oxidative degradation of the double bond generated there is carried out to them by $KMnO_4$ and the method of obtaining a COO group content fluoride copolymer is indicated, By this method, the fluoride oligomer which has a carboxyl group thoroughly in the both ends of a main chain was not obtained, but there was a problem that processes, such as removal of heavy metal Mn, were moreover needed.
[0003]To "a functional fluorine-containing polymer" (the 11-12th page, 1982, Nikkan Kogyo Shimbun issue). Copolymerization of the $CF_2=CFO(CF_2)_4COOCH_3$ is carried out to tetrafluoroethylene, and it is indicated that the fluoride oligomer which has an ester group in a side chain can be manufactured. This side-chain ester group is hydrolyzed and the method of manufacturing the fluoride oligomer which contains a carboxyl group in the side chain of oligomer is indicated. However, by such a method, the ester group content monomer which cannot obtain the fluoride oligomer which has a carboxyl group in the both ends of a main chain, and is used for this copolymerization reaction is very expensive, and it is not suitable for industrial use. Since the hydrolysis reaction of an ester group did not fully advance unless it is under an

alkali condition, there was a problem of being hard to apply in a vinylidene fluoride system copolymer.
[0004]By the way, the vulcanized gum waste represented by the barricade generated at the time of the vulcanization molding of rubber, Even if it reproduces and uses this in the case of common rubber, it is deficient in a cost merit, but if the high fluorocarbon rubber of a material cost has, use of the vulcanized gum waste has been important problem also from a point of cost reduction. Therefore, the both ends of the main chain were expected the appearance of the manufacturing method of the fluoride oligomer which has a carboxyl group by reuse of such vulcanization fluorocarbon rubber waste.
[0005]If it is in the reproducing method of the vulcanization fluorocarbon rubber which is performed conventionally and which constructed the bridge, Further the method or it which grinds and plasticizes a barricade, waste, etc. mechanically Nitric acid, The method of processing by potassium permanganate, various amine, etc. is used, and [JP,59-217734,A, A 59-217735 gazette, the US,3,291,761,B Description, German patent application public presentation Description 2 360 927 -- said -- 2 420 993, Kautschuk+Gummel-Kunststoffe23. Jahrgang, and Heft 3/1976 -- 218 pages, The 45. Jahrgang, Nr. 9/92, 742 pages, Proizvo Shin, Rezinotekhn; Asbestotekhn. Izdlii (Moskva) 1979, six volumes, and 7page], The obtained recycled article is blended with virgin rubber (new rubber) like a filler, and is used as a kind of extender.
[0006] However, in order to acquire reproduction fluorocarbon rubber from the vulcanization fluorocarbon rubber which constructed the bridge. From the vinylidene fluoride structure of the vinylidene fluoride copolymer which must decompose the structure of cross linkage and is generally used as fluorocarbon rubber. Even if it was hard to apply the decomposing method under basic conditions and strong acid, such as nitric acid, was used for the structure of cross linkage by a polyhydroxy compound (polyol), the problem of decomposition not progressing was among the degrees which can reproduce a part for rubber and can isolate.
[0007][0007]. In rubber, in almost all those cases, allot and it is at vulcanization which constructed the bridge.
Acquisition of the reproduction fluorocarbon rubber separated thoroughly rare ****** and such a filler.
There was also a problem that the above-mentioned reproducing method cannot be applied depending on the bridge construction system in the case of vulcanization fluorocarbon rubber formation. As coping with such problem and applicant of this application's being indicated to Tokuganhei10-150743 and Tokuganhei10-090856, While proposing the new fluoride oligomer (it may be called the following "main chain both-ends carboxyl group content fluoride oligomer") which contains a carboxyl group in the both ends of a main chain, The method of manufacturing the fluoride copolymer which contains a carboxyl group in the both ends of a main chain from this waste safely and at a low price was proposed by using vulcanization fluorocarbon rubber waste as a raw material.
[0008]That is, the vinylidene fluoride copolymer was processed with the base and the peroxide, and the method of manufacturing a carboxyl group content vinylidene fluoride copolymer was proposed. It is oligomer produced by carrying out decomposition treatment of the fluorocarbon rubber bridge construction thing, Separation with a filler etc. is easy because of solvent fusibility, and the main chain both-ends carboxyl group content fluoride oligomer which can be effectively used as chain length extension agents, such as an epoxy resin, isocyanate resin, and oxazoline resin, was proposed.
[0009]However, it could not say that the above main chain both-ends carboxyl group content fluoride

oligomer had a by no means quick cure rate of the hardenability constituent containing this fluoride oligomer, but there was a problem that a use or a curing process was limited. For this reason, the both ends of the main chain quick a cure rate and useful as raw materials, such as chain elongation agents, such as an epoxy resin and isocyanate resin, or solvent resistance sealant, adhesives, and a paint, are expected the appearance of fluoride oligomer which has functional groups, such as an ester group, and a manufacturing method for the same.

[0010]

[Objects of the Invention]This invention is what is going to solve the problem accompanying the above conventional technologies, It aims at providing the hardenability constituent excellent in the cure rate which becomes both ends of the main chain excellent in the cure rate from the fluoride oligomer which has functional groups, such as an ester group, its manufacturing method, this fluoride oligomer, etc.

[0011]

[Summary of Invention]A number average molecular weight is fluoride oligomer which is 1000-10000, and main chain both-ends ester group content fluoride oligomer concerning this invention is characterized by having an ester group in the both ends of the main chain of this fluoride oligomer. A number average molecular weight is fluoride oligomer which is 1000-10000, and main chain both-ends unsaturation group content fluoride oligomer concerning this invention is characterized by having an unsaturation group in the both ends of the main chain of this fluoride oligomer. A number average molecular weight is fluoride oligomer which is 1000-10000, and main chain both-ends alcoholic hydroxyl group content fluoride oligomer concerning this invention is characterized by having an alcoholic hydroxyl group in the both ends of the main chain of this fluoride oligomer. As for such fluoride oligomer, it is preferred that it is a copolymer containing the repeating unit derived from vinylidene fluoride.

[0012]The manufacturing method of main chain both-ends unsaturation group content fluoride oligomer concerning this invention is characterized by making said main chain both-ends ester group content fluoride oligomer and unsaturation group content amine react below 60 **. The manufacturing method of main chain both-ends alcoholic hydroxyl group content fluoride oligomer concerning this invention is characterized by making said main chain both-ends ester group content fluoride oligomer and alcoholic hydroxyl group content amine react below 60 **.

[0013]The hardenability constituent concerning this invention is characterized by consisting of said main chain both-ends unsaturation group content fluoride oligomer, an acrylic monomer (meta), and a photopolymerization initiator. The hardenability constituent concerning this invention is characterized by consisting of said main chain both-ends unsaturation group content fluoride oligomer, an acrylic monomer (meta), and a radical generator. The hardenability constituent concerning this invention is characterized by consisting of said main chain both-ends alcoholic hydroxyl group content fluoride oligomer and a polyisocyanate compound.

[0014]

[Detailed Description of the Invention]Hereafter, main chain both-ends functional group content fluoride oligomer concerning this invention, its manufacturing method, and a hardenability constituent are explained concretely.

As main chain both-ends functional group content oligomer of main chain both-ends functional group content fluoride oligomer this invention, main chain both-ends ester group content fluoride oligomer, main

chain both-ends unsaturation group content fluoride oligomer, and main chain both-ends alcoholic hydroxyl group content fluoride oligomer are mentioned. Since such main chain both-ends functional group content fluoride oligomer is obtained from main chain both-ends carboxyl group content fluoride oligomer, it explains main chain both-ends carboxyl group content fluoride oligomer first.

[0015]The fluoride oligomer which has a carboxyl group in the both ends of the main chain used as the starting material of main chain both-ends carboxyl group content fluoride oligomer this invention is obtained by carrying out decomposition treatment of the fluorocarbon rubber over which the bridge was constructed by the method indicated, for example to Tokuganhei10-150743. The fluorocarbon rubbers used as such a raw material are wastes, such as a barricade at the time of carrying out vulcanization molding by a polyol, amine, or peroxide, waste, and poor mold goods. The fluoride oligomer which newly has a carboxyl group in the both ends of a main chain from fluorocarbon rubber may be compounded.

[0016]Especially if it is the fluorocarbon rubber containing fluoride as a fluorocarbon rubber bridge construction thing by which vulcanization molding was carried out, it will not be limited, but a copolymer with vinylidene fluoride, other fluorine-containing olefins, or an olefin is mentioned, for example. As a copolymer containing vinylidene fluoride, specifically, Vinylidene fluoride, tetrafluoroethylene, a hexafluoro propene, Perfluoro, such as chlorotrifluoroethylene, a pentafluoro propene, and perfluoro (methyl vinyl ether) (alkyl vinyl ether), Copolymers at least with a kind, such as propylene, fluoridation vinylidene-hexafluoro propene-tetrafluoroethylene the copolymer of 3 yuan, Fluoridation vinylidene-tetrafluoroethylene propylene copolymer of 3 yuan, fluoridation vinylidene-tetrafluoroethylene perfluoro (methyl vinyl ether) copolymer of 3 yuan, etc. are mentioned.

[0017]As a fluorocarbon rubber bridge construction thing by which vulcanization molding was carried out, Tetrafluoro ethylene propylene rubber, a tetrafluoroethylene perfluoro (methyl vinyl ether) copolymer, Tetrafluoroethylene copolymers, such as tetrafluoroethylene perfluoro (methyl vinyl ether)-ethylene a copolymer of 3 yuan, etc., etc. are mentioned. As these various copolymers, that to which copolymerization of the cross-linking group content monomers, such as bromine and/or an iodine content compound, a nitrile group, a glycidyl group, a hydroxyalkyl group, and a perfluoro phenyl group, was carried out can also be used into a copolymer.

[0018]After being immersed one day or more into an organic solvent and fully swelling an organic solvent in a fluorocarbon rubber bridge construction thing, decomposition treatment of these fluorocarbon rubber bridge construction things is carried out. As such an organic solvent, if a fluorocarbon rubber bridge construction thing may be swollen, can use arbitrary things, but. For example, amide, such as ketone, dimethylformamide, and dimethylacetamide. Halogen-containing compounds, such as sulfur containing compounds, such as dimethyl sulfoxide and sulfolane, alcohols, lower fatty acid, ester species, trichlorofluoroethane, hexafluoro isopropanol, trifluoroethanol, and trichloroacetic acid, etc. are used.

[0019]Decomposition treatment of the fluorocarbon rubber bridge construction thing after swelling is performed under existence of a base and a peroxide. Specifically as a base, hydroxide of an alkaline metal, carbonate, organic acid salt, tertiary amine, the 3rd class phosphine, etc. are used. Specifically as a peroxide, hydrogen peroxide, persulfate, peracetic acid, organic peroxide, organic hydroperoxides, etc. are mentioned. Among these, hydrogen peroxide is preferred especially from a cost aspect. Addition of a base and a peroxide is the turn of a peroxide and a base, can be performed at once or can be performed in several steps.

[0020] When carrying out decomposition treatment of the fluorocarbon rubber bridge construction thing distributed by the latex state, in order to raise decomposition treatment speed, When swelling the fluorocarbon rubber bridge construction thing distributed by the latex state with an organic solvent, it is usually preferred as a catalyst to use the 4th class phosphonium salt, such as quarternary ammonium salt or the 4th class onium salt. Although decomposition treatment is usually performed at the temperature of about 0-100 ** and there is no restriction in particular, it is preferred to be carried out at about 10-30 ** from a viewpoint of exothermic control. The molecular weight and acid value of a decomposition product can be arbitrarily adjusted by introducing the double bond by a base.

[0021]Phase splitting is carried out with strong chloride, a coarse packing material portion is first separated using a filter, the penetrant remover and filtrate are set, it adds to underwater [ a lot of ], and the fluorocarbon rubber bridge construction thing by which decomposition treatment was carried out settles decomposition treatment output, and is agitated violently for a long time. If the output acquired will be dried about three days at about 65 ** after repeating such operation 3 times - 5 times and making it precipitate whenever [ re-], the fluoride oligomer which contains a carboxyl group in the both ends of a main chain can be obtained. The fluoride oligomer which contains a carboxyl group only in one end of a main chain can also be made to generate in addition to the fluoride oligomer which is low on the structure of decomposition as for the probability which the fluoride oligomer which has three or more ends generates, and contains a carboxyl group in the both ends of a main chain.

[0022]In main chain both-ends ester group content fluorination oligomer this invention, the main chain both-ends carboxyl group content fluoride oligomer produced by performing it above is dissolved and esterified by an organic solvent. Esterification of main chain both-ends carboxyl group content fluoride oligomer is performed, for example by esterifying main chain both-ends carboxyl group content fluoride oligomer and alcohol under existence of an acid catalyst and in a solvent.

[0023]As alcohol, fatty alcohol of the carbon numbers 1-5 and aromatic alcohol of the carbon numbers 6-12 are mentioned. Specifically, aromatic alcohol, such as fatty alcohol, such as methanol, ethanol, n-propyl alcohol, and isopropyl alcohol, and benzyl alcohol, is mentioned. Specifically as a solvent, ketone, alcohols, lower fatty acid, ester species, and halogen-containing compounds are mentioned.

[0024]Specifically as an acid catalyst, concentrated sulfuric acid, chloride, p-toluenesulfonic acid, an acetic anhydride, anhydrous triphloroacetic acid, etc. are mentioned. Such an acid catalyst is preferably used in 3 to 5weight % of quantity one to 10weight % to 100 weight % of main chain both-ends carboxyl group content fluoride oligomer. Generally the reaction temperature of such esterification of main chain both-ends carboxyl group content fluoride oligomer is 0 ** - 150 **.

They are 70 ** - 120 ** preferably.

Such a reaction is usually performed for 1 to 5 hours, and it is carried out preferably for 2 to 3 hours.

[0025]A solvent is distilled off after ending reaction. Since the purity of a resultant will become low if there is little quantity to distill off at this time, and a resultant will become hyperviscosity if too large, 50 to 90% of the quantity of the solvent to distill off is desirable, and it is especially preferred that it is 70 to 80%. After introducing the melted object which includes the acquired resultant after distilling off a solvent into a lot of water and settling a resultant, it stirs violently. In this case, as for water, it is preferred that they are about 5 to 50 times to a resultant. After churning, after filtering and collecting resultants, it adds in a lot of water again, and this sediment is agitated violently. Such operation is usually performed about 3 to 10 times, and

a resultant is settled. Thus, if the obtained sediment is dried at about 40-80 **, the fluoride oligomer (it may be called the following "main chain both-ends ester group content fluoride oligomer") which has an ester group in the both ends of a main chain will be obtained.

[0026]Specifically as an ester group of the obtained main chain both-ends ester group content fluorination oligomer, methyl ester, ethyl ester, n-propyl ester, isopropyl ester, benzyl ester, etc. are mentioned. Such main chain both-ends ester group content fluorination oligomer is fluoride oligomer the ranges of whose number average molecular weight are 1000-10000.

[0027]The main chain both-ends ester group content fluoride oligomer from which it is obtained in the case of the copolymer in which the fluorocarbon rubber bridge construction thing used as a raw material includes the repeating unit derived from vinylidene fluoride is fluoride oligomer containing the repeating unit derived from vinylidene fluoride. Also about the case of the fluoride oligomer to which a starting material contains a carboxyl group in one end of a main chain. By the method of esterifying the fluoride oligomer which contains a carboxyl group in the both ends of the aforementioned main chain, and the same method, main chain one end carboxyl group content fluoride oligomer can be esterified, and main chain one end ester group content fluoride oligomer can be obtained.

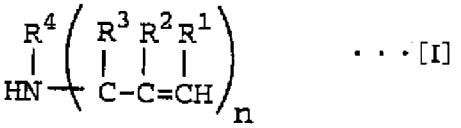
[0028]The main chain both-ends ester group content fluoride oligomer which is main chain both-ends unsaturation group content fluorination oligomer and the main chain both-ends alcoholic hydroxyl group content fluorination oligomer above, and was produced by making, Make unsaturation group content amine or alcoholic hydroxyl group content amine, such as an allyl group, react, and it amidates, To the both ends of a main chain, an unsaturation group. The fluorination oligomer (it may be called the following "main chain both-ends alcoholic hydroxyl group content fluoride oligomer") which contains an alcoholic hydroxyl group in the both ends of the fluorination oligomer (it may be called the following "main chain both-ends unsaturation group content fluoride oligomer") to contain or a main chain is obtained.

[0029]Main chain both-ends ester group content fluoride oligomer is specifically dissolved in a solvent, In this solution, the amine which has an unsaturation group or an alcoholic hydroxyl group can be added and amidated, and the fluorination oligomer which contains an alcoholic hydroxyl group in the both ends of the fluorination oligomer which contains an unsaturation group in the both ends of a main chain, or a main chain can be obtained. As such a solvent, acetone, a tetrahydrofuran, methyl ethyl ketone, methanol, ethanol, n-propyl alcohol, etc. are mentioned.

[0030]Amine containing an unsaturation group is following general formula [I].

[0031]

[Chemical formula 1]

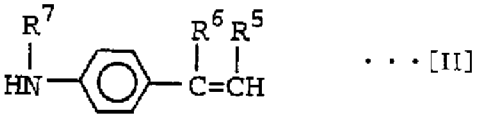


· · ·[I]

[0032] [$R^1$, $R^2$, $R^3$, and $R^4$ are an alkyl group with a hydrogen atom and 1-2 carbon atoms, or a phenyl group independently among a formula, respectively, and n is an integer of 1 or 2]. Or following general formula [II]

[0033]

[Chemical formula 2]



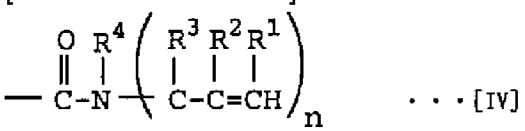
・・・[II]

[0034] [0034]. It is an unsaturation expressed with [the inside of a formula, $R^5$ and $R^6$ **, and $R^7$ are alkyl groups with a hydrogen atom and 1-2 carbon atoms independently, respectively].
Are Min and as amine of general formula [I] specifically, Allylamine, diaryl amine, a 3-amino-1-methyl-1-propene, A 3-amino-1-ethyl-1-propene, a 3-amino-1-n propyl-1-propene, A 3-amino-1-phenyl-1-propene, a 3-amino-2-methyl-1-propene, A 3-amino-2-ethyl-1-propene, a 3-amino-2-n propyl-1-propene, A 3-amino-2-phenyl-1-propene, a 3-amino-3-methyl-1-propene, A 3-amino-3-ethyl-1-propene, a 3-amino-3-n propyl-1-propene, A 3-amino-3-phenyl-1-propene, an N-methyl-3-amino-1-propene, An N-ethyl-3-amino-1-propene, an N-phenyl-3-amino-1-propene, a N-n propyl-3-amino-1-propene, etc. are mentioned, and, specifically, they are p-amino-still benzene, N-methyl-p amino-still benzene, etc. as amine of general formula [II].

[0035]Amine containing an alcoholic hydroxyl group is following general formula [III].
[0036]
[Chemical formula 3]

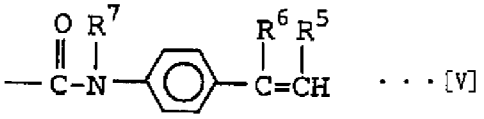
・・・[III]

[0037] An aliphatic series system alkyl group with 2-5 carbon atoms and $R^9$ among [type $R^8$ An aliphatic series system alkyl group with 1-3 carbon atoms, Or are amine which is expressed with] which is a phenyl group and which has an alcoholic hydroxyl group, and specifically, Ethanolamine, N-methyl-ethanolamine, N-phenyl-ethanolamine, N-phenyl-n-propanolamine, N-phenyl-n-butanol amine, etc. are mentioned.
[0038]As for such amine, it is desirable to use 2-5 mol in the quantity of 2-3 mol preferably especially to 1 mol of main chain both-ends ester group content fluoride oligomer. Reaction temperature of main chain both-ends ester group content fluoride oligomer, and unsaturation group content amine or alcoholic hydroxyl group content amine is usually performed at -10-60 **, and is preferably performed at 0 ** - 40 **.
[0039]A solvent is removed after ending reaction, it dries at about 30-50 ** for 10 to 30 hours, and the fluoride oligomer which contains an unsaturation group or an alcoholic hydroxyl group in the both ends of a main chain is obtained. The functional group of the both ends of the fluoride oligomer which has an unsaturation group in the both ends of a main chain is following general formula [IV] or [V].
[0040]
[Chemical formula 4]



・・・[IV]

[0041]
[Chemical formula 5]

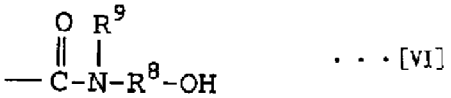


[0042] It is expressed with [the inside of a formula, $R^1$, $R^2$, $R^3$, $R^4$, n, $R^5$, $R^6$, and $R^7$ are synonymous with $R^1$ of the above-mentioned general formula [I] and [II], $R^2$, $R^3$, $R^4$, n, $R^5$, $R^6$, and $R^7$ respectively]. Such main chain both-ends unsaturation group content fluorination oligomer is oligomer in which a number average molecular weight has a value of 1000-10000.

[0043]The functional group of the both ends of the fluoride oligomer which has an alcoholic hydroxyl group in the both ends of a main chain is following general formula [VI].

[0044]

[Chemical formula 6]



[0045] It is expressed with [the inside of a formula, $R^8$, and $R^9$ are synonymous with $R^8$ of the above-mentioned general formula [III], and $R^9$ respectively]. Such main chain both-ends alcoholic hydroxyl group content fluorination oligomer is oligomer in which a number average molecular weight has a value of 1000-10000.

[0046]the base from which such main chain both-ends unsaturation group content fluorination oligomer and main chain both-ends alcoholic hydroxyl group content fluorination oligomer became a raw material -- in the case of the copolymer in which a rubber bridge construction thing contains vinylidene fluoride, it is fluoride oligomer containing the repeating unit derived from vinylidene fluoride. When the aforementioned main chain one end ester group content fluoride oligomer is used as a starting material, The amidation reaction of said main chain both-ends ester group content fluoride oligomer is carried out with unsaturation group content amine or alcoholic hydroxyl group content amine, By the method of obtaining main chain both-ends unsaturation group content fluoride oligomer or main chain both-ends alcoholic hydroxyl group content fluoride oligomer, and the same method. Main chain one end ester group content fluoride oligomer can be amidated, and main chain one end unsaturation group content fluoride oligomer or main chain one end alcoholic hydroxyl group content fluoride oligomer can be obtained.

Hardenability constituent (i) Main chain both-ends unsaturation group content fluoride oligomer (it may be called the following "fluoride oligomer (A)") produced by making it above, A hardenability constituent can be obtained from the acrylic monomer (meta) (C) as reactive diluent, and a photopolymerization initiator (D) or a radical generator (E).

[0047][0047]. - (A) of such a fluoride cage is 20 to 100 weight % of hardenability constituents.

** which is quantity % and is more preferably used in 50 to 70weight % of quantity.

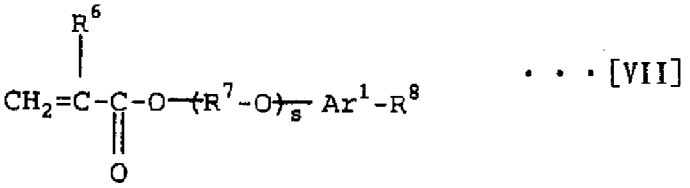
(ii) A hardenability constituent can be obtained from the main chain both-ends alcoholic hydroxyl group content fluoride oligomer (it may be called the following "fluoride oligomer (B)") produced by making it above, and polyisocyanate compound (I).

[0048][0048]. - (B) of such a fluoride cage is 20 to 100 weight % of hardenability constituents.
** which is quantity % and is more preferably used in 50 to 70weight % of quantity.
In this invention, it faces obtaining such a hardenability constituent and other reactive diluent, other hardening agents (F), inorganic matter / organic paints (G), and other additives (H) are used suitably.
[0049]In reactive diluent this invention, when preparing the hardenability constituent which consists of fluoride oligomer (A), it is preferred to blend a diluent. It is because the fluoride oligomer which has a functional group in the both ends of a main chain has high viscosity, so processing operation of mixing with fluorination oligomer (A), paints, or a filler, the coating of a hardenability constituent, pouring, etc. is not easy as it is. As such a diluent solvent, reactive diluent is used preferably. Reactive diluent is especially used preferably, when preparing a hardening constituent with a photopolymerization initiator and/or a radical generator using fluoride oligomer (A).
[0050]As such reactive diluent, an acrylic monomer (meta) (C) is preferred in respect of a cure rate. If fluoride oligomer (A) is dissolved, all of such (meta) an acrylic monomer are usable. Monofunctional nature or polyfunctional any acrylic monomer (meta) can be used. As such (meta) an acrylic monomer, Specifically, as for mono- **** of di(meth)acrylate and the alkylene oxide adduct of a polyol, as for the acrylate (meta) of alkoxy alkylene glycol, and mono- **** of alkylene glycol, poly(meta) acrylate etc. are mentioned.
[0051]As acrylate (meta) of alkoxy alkylene glycol, the mono- (meta) acrylate of methoxy ethylene glycol, the mono- (meta) acrylate of an ethoxyethylene glycol, etc. are mentioned. As for mono- **** of di(meth) acrylate and propylene glycol, as for mono- **** of ethylene glycol, di(meth)acrylate etc. are mentioned [ mono- **** of alkylene glycol ] as di(meth)acrylate.
[0052]In poly(meta) acrylate, mono- **** of the alkylene oxide adduct of a polyol as a polyol, Alkylene glycol, such as ethylene glycol and propylene glycol, The polyol which has four or more hydroxyl groups, such as triol, such as trimethylolethane, trimethylolpropane, and glycerin, pentaerythritol, and dipentaerythritol, is mentioned. As alkylene oxide, ethyleneoxide, propylene oxide, butylene oxide, etc. are mentioned. As the number of addition mols of the alkylene oxide concerned, 1-10 mol is preferred. As an example of the acrylate concerned (meta), Di(meth)acrylate and tetraethylene glycol mono- **** diethylene-glycol mono- **** Di(meth)acrylate, As for dipropylene glycol mono- ****, mono- **** of polyalkylene glycols, such as di(meth)acrylate, mono- **** of di(meth)acrylate and tripropylene glycol Di(meth)acrylate, And trimethylolpropane bird (meta) acrylate, pentaerythritol tri(meta)acrylate, Ethyleneoxide or propylene oxide denaturation objects, such as pentaerythritol tetra (meta) acrylate and dipentaerythritol hexaacrylate, etc. are mentioned.
[0053]Such reactive diluent can also use two or more sorts together. Within limits which do not have an adverse effect on the reactive resin obtained eventually. Alkyl (meta) acrylate, such as methyl (meta) acrylate, ethyl (meta) acrylate, and propyl (meta) acrylate, Reactive diluent, such as trimethylolpropane bird (meta) acrylate, pentaerythritol tri(meta)acrylate, pentaerythritol tetra (meta) acrylate, and dipentaerythritol hexaacrylate, is also mixable.
[0054]As reactive diluent, monofunctional nature and a polyfunctional (meta) acrylic monomer can also be used. As a monofunctional nature monomer, specifically Acrylamide, 7-amino-3,7-dimethyloctyl (meta) acrylate, Isobutoxymethyl(meta) acrylamide, isobornyl oxyethyl (meta) acrylate, Isobornyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Ethyldiethylene-glycol (meta) acrylate, t-octyl(meta) acrylamide, (Meta)

Acryloyl morpholine, diacetone (meta) acrylamide, N and N-dimethylaminoethyl (meta) acrylate, N, and N-diethylaminoethyl (meta) acrylate, Lauryl (meta) acrylate, dicyclopentadiene (meta) acrylate, JISHIKURO pentenyloxyethyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, N,N-dimethyl(meta) acrylamide tetra chlorophenyl (meta) acrylate, 2-tetrachlorophenoxyethyl (meta) acrylate, tetrahydrofurfuryl (meta) acrylate, tetrabromo phenyl (meta) acrylate, 2-tetrabromo phenoxyethyl (meta) acrylate, 2-trichlorophenoxy ethyl (meta) acrylate, tribromophenyl (meta) acrylate, 2-tribromophenoxyethyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, phenoxyethyl (meta) acrylate, Butoxyethyl (meta) acrylate, pentachlorophenyl (meta) acrylate, Pentabromophenyl (meta) acrylate, polyethylene-glycol mono- (meta) acrylate, Polypropylene-glycol mono- (meta) acrylate, bornyl (meta) acrylate, methyl bird ethylene diglycol (meta) acrylate and following general formula [VII] - [IX]

[0055]

[Chemical formula 7]

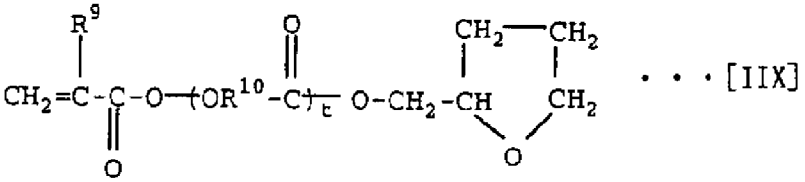


・・・[VII]

[0056] $R^6$ expresses a hydrogen atom or a methyl group among [type -- $R^7$ -- the carbon numbers 2-6 -- it being an alkylene group of 2-4 preferably, and, $R^8$ -- a hydrogen atom or the carbon numbers 1-12 -- it is an alkyl group of 1-9 preferably, and $Ar^1$ is a divalent aromatic group of a phenylene group, a biphenylene group, a naphthylene group, etc. -- s -- 0-12, and] that is the number of 1-8 preferably

[0057]

[Chemical formula 8]

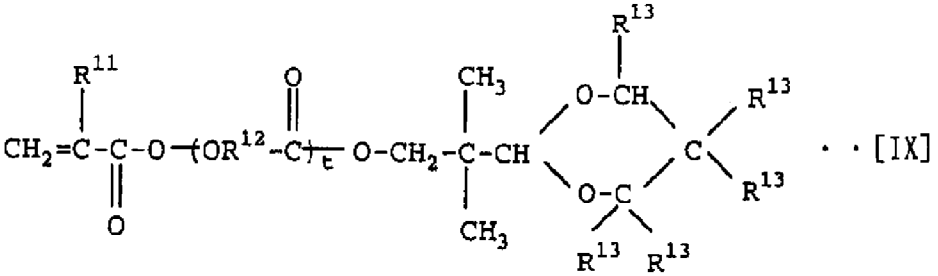


・・・[IIX]

[0058] [-- $R^9$ expresses a hydrogen atom or a methyl group among a formula -- $R^{10}$ -- 2-8 carbon atoms -- it is an alkylene group of 2-5 preferably -- t -- 1-8, and] that is the number of 1-4 preferably

[0059]

[Chemical formula 9]



・・[IX]

[0060] $R^{11}$ expresses a hydrogen atom or a methyl group among [type -- $R^{12}$ -- 2-8 carbon atoms -- it

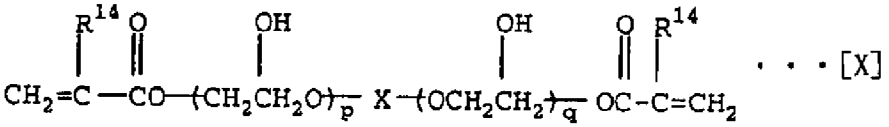
being an alkylene group of 2-5 preferably, and, $R^{13}$ expresses a hydrogen atom or a methyl group -- t -- 1-8 -- it being the number of 1-4 preferably, and, Two or more $R^{13}$ can mention vinyl group content monomers, such as acrylyl group (meta) content monomer;N-vinylcarbazole, such as a compound expressed with] which may be the same or may differ, N-vinyl pyrrolidone, and N-vinylcaprolactam.

[0061]These monofunctional nature monomers are ARONIX M-111, M-113, and M-117 (above), for example. Things marketed, such as the Toagosei make, KAYARAD TC110S, R-629, R-644 (above, Nippon Kayaku Co., Ltd. make), and the screw coat 3700 (made by OSAKA ORGANIC CHEMICAL INDUSTRY, LTD.), can also be used. Especially when using a monofunctional nature monomer, N-vinyl pyrrolidone, N-vinylcaprolactam, and acryloyl morpholine are [ among these ] preferred.

[0062]As a polyfunctional monomer, for example Ethylene glycol di(metha)acrylate, JISHIKUROPENTENIRUJI (meta) acrylate, triethylene glycol diacrylate, Tetraethylene glycol di(metha) acrylate, tricyclodecane diyl JIMECHI range (meta) acrylate, Bird methylol pro pansy (meta) acrylate, trimethylolpropane bird (meta) acrylate, EO denaturation trimethylolpropane bird (meta) acrylate, PO denaturation trimethylolpropane bird (meta) acrylate, Tripropylene glycol di(meta)acrylate, neopentyl glycol di(metha)acrylate, 1, 4-butanediol di(metha)acrylate, 1,6-hexanediol di(metha)acrylate, Pentaerythritol tri (meta)acrylate, polyester TERUJI (meta) acrylate, polyethylene glycol di(meta)acrylate, tris [(meta) acryloxyethyl] isocyanurate, and following general formula [X]

[0063]

[Chemical formula 10]



$$CH_2=C(R^{14})-CO-(CH_2CH_2O)_p-X-(OCH_2CH_2)_q-OC-C(R^{14})=CH_2 \quad \cdots [X]$$

[0064] $R^{14}$ expresses a hydrogen atom or a methyl group among [type -- X -- the carbon numbers 2-6 -- desirable -- the alkylene group of 2-4. It is a divalent basis of a phenylene group, a biphenylene group, a naphthylene group, etc., and p and q can mention acrylyl group (meta) content monomers, such as acrylyl group (meta) content monomers, such as a compound independently expressed with 1-10, and] that is the number of 1-5 preferably, respectively.

[0065]Especially when using a polyfunctional monomer, among these Tris (meta) (acryloxyethyl) isocyanurate, Trimethylolpropane triacrylate, EO denaturation trimethylolpropane triacrylate, Tricyclodecane diyl JIMECHI range (meta) acrylate, tetraethylene glycol di(metha)acrylate, Tripropylene glycol di(meta)acrylate, neopentyl glycol di(metha)acrylate, polyethylene glycol di(meta)acrylate, and the acrylyl group content monomer expressed with said formula [IIX] (meta) are preferred.

[0066]As a polyfunctional monomer, specifically, YUPIMA UV, SA1002 (above, Mitsubishi Chemical make), the screw coat 700 (above) The OSAKA ORGANIC CHEMICAL INDUSTRY, LTD. make, KAYARAD R-604, D-310, D-330 (above) The Nippon Kayaku Co., Ltd. make, ARONIX M-210, M-315 (above) the Toagosei make, epoxy ester 40EM, 70PA, 200PA, 1600A, 80MFA, 3002M, 3002A, 3000M and 3000A, 200EA, 400EA (above, product made from Kyoeisha Chemistry), etc. -- etc. -- the monomer marketed can also be used.

[0067]The above-mentioned monofunctional nature and a polyfunctional monomer are one-sort

independent, or can be combined two or more sorts and can be used. In addition, the acrylate monomer which has polyester in a side chain (meta) is also used preferably. For example, omega-carboxy polycaprolactone monoacrylate (M-5300, Toagosei make), An acrylic acid dimer (M-5600, Toagosei make), The plaque cells F, FD, and FMA, such as polyester acrylates (above M-6100, M-6200, M-6250, M-6500, M-7100, M-8030, M-8060, M-8100, M-8530, M-8560, M-9050, Toagosei make). DC (above, Daicel Chemical Industries, Ltd.) etc. are mentioned.

[0068]When aiming at improvement in the mechanical physical property of a hardenability constituent especially, the acrylate named urethane acrylate generically can also be used. Specifically, they are following general formula [XI] and [XII].

$CH_2$=CHCOOR'OCONH-(R-NHCOO-[polyol]-OCONH) $_n$- R-NHCOOR'OCOCH=$CH_2$ ... [XI]

Or $CH_2$=CHCOOR'OCONH-(R-NHCOO-[polyol]-OCONH) $_n$ - [Polyol]-OH ... [XII]

The acrylate (M-1100, 1200, 1210, 1310, 1600 (made by Toagosei), etc.) expressed with [R and R' expresses the alkyl group of the carbon numbers 1-5 mutually-independent among a formula] is mentioned.

[0069]In said general formula [XI] and [XII], a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl group, t-butyl group, n-pentyl group, i-pentyl group, etc. can be mentioned as an alkyl group of the carbon numbers 1-5, for example. The alkyl group of the carbon numbers 1-3 is [ among these ] preferred. Such reactive diluent can be independent one sort, or can be combined two or more sorts, and can also be used.

[0070]As for such reactive diluent especially, in this invention, it is preferred to blend in 30 to 50weight % of quantity 20 to 75weight % to 100 weight % of hardenability constituents. It is easy to produce the inconvenience that the dent-proof nature of a hardenability constituent will fall easily if 75 weight % is exceeded, and repetition printing endurance falls easily. If less than 20 weight %, the viscosity of a hardenability constituent will increase and it will become difficult to perform processing operation of the coating of a hardenability constituent, pouring, etc.

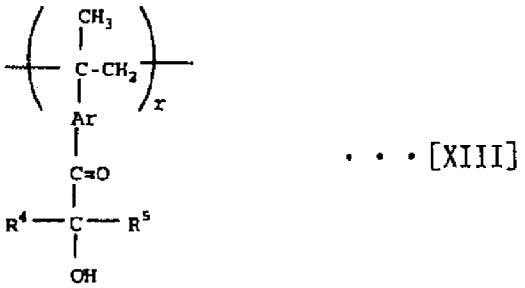
[0071] A photopolymerization initiator can be blended with the hardenability constituent which consists of fluorination oligomer (A) by photopolymerization initiator (D) this invention. As a photopolymerization initiator, if an optical exposure decomposes, a radical is generated and a polymerization is made to start, any may be sufficient and a sensitizer can also be used further if needed. "Light" means ultraviolet rays, visible light, etc. here. When performing hardening by an electron beam, it is not necessary to blend a photopolymerization initiator.

[0072]As such a photopolymerization initiator, specifically, 1-hydroxycyclohexylphenyl ketone, a 2,2-dimethoxy- 2-phenylacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-(4-isopropylphenyl)-2-hydroxy-isobutane 1-one, 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl- 4-methoxybenzophenone, 1-(4-dodecylphenyl)-2-hydroxy-isobutane 1-one, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino propan-1-one, 2,4,6-trimethyl benzoyl diphenylphosphine oxide, Ethyl-2,4,6-trimethyl benzoylphenyl phosphinate, Bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide, Screw acyl phosphine oxide, methylbenzoyl formate, 4-benzoyl-4'-methyldi phenyl sulfide, benzyl dimethyl ketal, a fluorenone, a fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, a Michler's ketone. 2-benzyl-2-dimethylamino 1 -(4-morpholinophenyl)- Butan-1-one, An acetophenone, 3-methylacetophenone,

benzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, 3,3',4,4'-tetra(t-butyl par oxycarbonyl) benzophenone (BTTB), Acetophenone benzyl ketal, a triphenylamine, carbazole, 4-chlorobenzo phenon, anthraquinone, xanthone, diethylthio xanthone, 2-isopropyl thioxanthone, 4-isopropyl thioxanthone, Combination with 2-chloro thioxanthone, 1-chloro-4-propoxy thioxanthone, and BTTB and dye sensitizing agent;, for example, a xanthene, thoxanthene, a coumarin, a keto coumarin, etc., etc. are mentioned. Following general formula (XIII)

[0073]

[Chemical formula 11]



・・・[XIII]

[0074] [$R^4$ and $R^5$ are the alkyl groups of the carbon numbers 1-5 mutually-independent among a formula, Ar is a divalent aromatic group of a phenylene group, a biphenylene group, a naphthylene group, etc., and r can also use the compound expressed with 2-50, and] that is the number of 2-20 preferably. In said general formula [XIII], a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl group, t-butyl group, n-pentyl group, i-pentyl group, etc. can be mentioned as an alkyl group of the carbon numbers 1-5, for example. The alkyl group of the carbon numbers 1-3 is [ among these ] preferred.

[0075]Especially among these Benzyl dimethyl ketal, benzophenone, 1-hydroxycyclohexylphenyl ketone, 2,4,6-trimethyl benzoyl diphenylphosphine oxide, Ethyl-2,4,6-trimethyl benzoylphenyl phosphinate, Bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane 1-one, 2-benzyl-2-dimethylamino 1 -(4-morpholinophenyl)- Butan-1-one etc. are preferred. As these commercial items, it is Irgacure 184, 651, 500, 907, 369, 784, and 2959 (above). The Ciba-Geigy make, Lucirin TPO, LR8893 (above) The BASF A.G. make, Darocur 1116, 1173 (above, Merck Co. make), YUBEKURIRU P36 (above, product made by UCB), ESCACURE KIP150, ESCACURE KIP100F (above, product made by LAMBERTI), etc. can be mentioned.

[0076]Especially in this invention, when making it harden by the exposure of ultraviolet rays, a photopolymerization initiator can be blended with a water dispersing element. As a photopolymerization initiator, the photopolymerization initiator of water solubility or hydrophilic nature is preferred, and specifically, DAROCUR 2959, 1173, and 116, IRGACURE 184, 261, 500, 651, 907, 369, 819, 1700, 2959, and 1173 (all are the products made from tiba speciality chemicals), The KANTA cures ABQ and BTC, QTX (all are the products made from shell chemistry), etc. are mentioned. In addition, benzoin, benzoin methyl ether, benzophenone, benzyl dimethyl ketal, 2,4-dimethyl thioxanthone, etc. which are usually used by the solvent system or the non-solvent system can be used.

[0077]Such a thing for which a photopolymerization initiator is used independently can also use two or more kinds together if needed. When using two kinds together, Concomitant use of 1-hydroxycyclohexylphenyl ketone and 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane 1-one or 2,4,6-trimethyl benzoyl diphenylphosphine oxide, and 2-methyl-1-[4-. (Methylthio) Concomitant use of

phenyl]-2-morpholinopropane 1-one is preferred.

[0078][0078]. Such ** and ******** are 0.01 preferably per total weight 100 weight section of a hardenability constituent.

It is a quantity part and is 0.03-6 especially preferably 0.02 to 8 weight section more preferably.

If ten weight sections are exceeded, it may have an adverse effect on the hardening characteristic of resin liquid, the physical properties of a hardened material, handling, etc., and in less than 0.01 weight section, a cure rate will become low and the tendency for productivity to fall will increase.

[0079]Before moisture powder or after moisture powder may be available for addition of a photopolymerization initiator. When using the photopolymerization initiator with small solubility to water especially by a solid, since it is easy to dissolve the photopolymerization initiator concerned underwater, adding before moisture powder is preferred. It is preferred to carry out evaporation scattering of ammonia or organic amine which is the water and the desirable neutralizer which are carrier fluid with heating before hardening. When moisture remains in a cured film, film strength may be insufficient or membranous transparency may be spoiled.

[0080]In radical generator (E) this invention, 2 liquid base resin type acrylic adhesives can also be blended and hardened as a radical generator when hardening the hardenability constituent which blended fluoride oligomer (A). The 1st liquid in which such 2 liquid base resin type acrylic adhesives use as the main ingredients the organic peroxide made to generate a polymerization nature (meta) acrylic monomer and a radical, It consists of the 2nd liquid that uses as the main ingredients the reducing agent which forms the organic peroxide and the redox catalyst system in a polymerization nature (meta) acrylic monomer and the 1st liquid, and, specifically, they are phosphorous acid or/and following general formula [XIV], [XV], and [XVI] in the 1st liquid.

[0081]

[Chemical formula 12]

・・・[XIV]

[0082] [-- $R_1$ is aryl group, alkyl-group [ of the carbon numbers 1-5 ], alkyl halide group, or $R_3OR_4$- (alkyl group of the carbon numbers 1-5 from which $R_3$ and $R_4$ are the same as or different) among a formula -- $R_2$ -- hydrogen or $R_1$]

[0083]

[Chemical formula 13]

・・・[XV]

[0084] [-- $R_5$ is an aryl group among a formula -- $R_6$ -- hydroxyl group or aryl group]

[0085]

[Chemical formula 14]

・・・[XVI]

[0086] [-- $R_7$ is an aryl group among a formula -- $R_8$ -- hydroxyl group or aryl group] -- from -- one sort of the acid phosphorus compounds chosen or two sorts or more contain, and 2 liquid base resin type acrylic adhesives, wherein the reducing agent in the 2nd liquid is a soluble vanadium compound are mentioned. As organic peroxide contained in the 1st liquid, t-butyl hydroperoxide, p-methane hydroperoxide, Hydroperoxide, such as a cumene hydroperoxide and diisopropylbenzene hydroperoxide. Peroxy ester species, such as t-butyl peroxy laurate, t-butyl peroxybenzoate, and t-butyl peroxide decanoate, etc. are suitable, and especially hydroperoxide is preferred.

[0087]As for the organic peroxide in such 1st liquid, it is preferably desirable as content in the 1st liquid to use in 7 to 10weight % of quantity one to 20weight %. As acid phosphorus compounds of the phosphorous acid contained in the 1st liquid or general formula [XIV], [XV], or [XVI], Monomethyl phosphate, dimethyl phosphate, monoethyl phosphate, Diethyl phosphate, monoisopropyl phosphate, diisopropyl phosphate, Monobutyl phosphate, dibutyl phosphate, mono-beta-chloroethyl phosphate, Di-beta-chloroethyl phosphate, mono-beta-bromoethyl phosphate, Di-beta-bromoethyl phosphate, monoethoxyethyl phosphate, Diethoxyethyl phosphate, monobutoxyethyl phosphate, Dibutoxyethyl phosphate, phenyl phosphate, diphenyl phosphate, phenylphosphonic acid, diphenylphosphonic acid, phenylphosphonous acid, diphenylphosphonous acid, etc. are mentioned, and one sort or two sorts or more of these mixtures are used.

[0088]0.5 to 7 weight % is preferably suitable for such acid phosphorus compounds 0.01 to 10weight % as content in the 1st liquid. Specifically as a soluble vanadium compound contained in the 2nd liquid, vanadyl acetylacetonate, vanadyl stearate, vanadium NAFUTENETO, vanadium acetylacetonate, vanadium benzoylacetonate, oxalic acid vanadyl, etc. are raised. As for these soluble vanadium compounds, 0.1 to 0.5 weight % is preferably used 0.01 to 1weight % as content in the 2nd liquid.

[0089]In order to raise the cure rate of the hardenability constituent which contains fluoride oligomer (A) and fluoride oligomer (B) in other hardening agent (F) this inventions, As a hardening agent, m-phenylene bis maleimide, 2,2-bis[4-(4-maleimide phenoxy) phenyl] propane, Bismaleimide, such as bis(3-ethyl-5-methyl-4-maleimide phenyl)methane, N,N'-(4,4'-diphenylmethane) bismaleimide, 1,3-cyclohexylene-bis-maleimide, and hexamethylene bismaleimide, can also be blended.

[0090]Hardening accelerators, such as ethylenetiourea, acetylthio urea, and benzoyl thiourea, can also be blended with these hardenability constituent as an additive agent for raising the cure rate of the hardenability constituent which contains fluoride oligomer (A) and fluoride oligomer (B). The amount of [ in the case used of blending such a hardening agent ] is 0.01 to 10 weight section preferably per total weight 100 weight section of a hardenability constituent.
It is 0.1 to 5 weight section more preferably.

[0091]In paints (G) this invention, inorganic or organic paints can be blended with the hardenability constituent with which fluoride oligomer (A) or fluoride oligomer (B) is blended by request. As an example of paints, white pigments, such as titanium oxide, a flower of zinc, lead white, RITOBON, and antimony

oxide, Black pigments, such as aniline black, iron black, and carbon black, the chrome yellow, Synthetic Ochre, titan yellow, and Hansa yellow (10G, 5G, and 3G.) In addition, yellow paints, such as benzine yellow and permanent yellow, Orange paints, such as the chromium vermilion, permanent orange, and Balkan first orange and an indanthrene brilliant orange, Brown pigments, such as iron oxide, permanent Brown, and Para Brown, Red ocher, cadmium red, antimony vermilion, Permanent Red, A rhodamine rake, an alizarin rake, thioindigo red, PV carmine, Red pigments, such as mono- light forced red and a KINAKU drine compounds system red pigment, Cobalt purple, manganese purple, forced violet, Violet Lake, Purple paints, such as indanthrene brilliant violet and dioxazine violet, ultramarine, Prussian blue, cobalt blue, an alkali blue rake, a peacock blue rake, a Victoria blue rake, non-metal copper phthalocyanine blue, copper copper phthalocyanine blue, Blue pigments, such as inda Indanthrene blue and indigo, chrome green, Chrome oxide, emerald green, naphthol green, green gold, Various kinds of fluorescent pigments, a metallic flake pigment, an extender, etc. besides green pigments, such as an acid green rake, a malachite green rake, Phthalocyanine Green, and a poly KURORU bromine copper phthalocyanine, are mentioned.

[0092]As for these paints, it is preferred to blend in the range of one to 50 weight section to the constituent except a photopolymerization initiator, and it is still more preferred to consider it as five to 30 weight section.

In other additive (H) this inventions, it is a range which does not bar functions of a hardening constituent, such as a cure rate or intensity of a hardenability constituent which contains fluoride oligomer (A) and fluoride oligomer (B), and other additives can be blended with a hardenability constituent. For example, liquid rubbers, such as a liquefied acrylonitrile butadiene copolymer, Impalpable powder polyethylene aiming at giving thixotropy, dibenzyliene-D-sorbitol, As what improves thixotropy grant agents, such as cellulose triacetate, octadecanamide, bentonite, and impalpable powder silicic acid, and the mothball stability in a room temperature, 2,6-di-tert-butyl-4-methylphenol, 2,2-methylene bis (4-methyl-6-t-butylphenol), Radical polymerization inhibitor, such as benzoquinone, hydroquinone, ethylenediaminetetraacetic acid 4 sodium, oxalic acid, N-methyl-N-nitrosoaniline, and N-nitrosodiphenylamine, etc. can also be blended by request.

[0093]In this invention, a hardenability constituent can also be diluted and used by an organic solvent if needed. If it is an organic solvent which dissolves fluoride oligomer (A), fluoride oligomer (B) and a photopolymerization initiator (D), and a radical generator (E) as an organic solvent, there will be no limitation in particular, but 50 ** - 200 ** of boiling points are the solvents which are 60 ** - 160 ** more preferably preferably. The solvent below 50 ** has the high danger of ignition, when carrying out dry removal of the organic solvent, after the boiling point's applying the constituent of this invention, and since it is easy to volatilize, it becomes difficult to control it of coating layer thickness. In the solvent in which the boiling point exceeds 200 **, since it is hard to volatilize, it becomes difficult to carry out dry removal of the organic solvent. As such an organic solvent, specifically Methanol, ethanol, Alcohols, such as isopropyl alcohol, butanol, and cyclohexanol, Aromatic hydrocarbon, such as ketone, such as ester species, such as ethyl acetate, butyl acetate, isoamyl acetate, and propionic acid-3-methoxymethyl, acetone, methyl ethyl ketone, and methyl isobutyl ketone, benzene, toluene, and xylene, etc. are mentioned. these solvents are independent -- it is -- two or more sorts can be used, combining.

[0094]As a desirable organic solvent, among these, ethanol, isopropyl alcohol, The partially aromatic solvent which consists of aromatic hydrocarbon, such as butanol and these alcohols solvents, acetate ester

system solvents, such as ethyl acetate and butyl acetate, propionic acid-3-methoxymethyl and toluene, and xylene, is mentioned. In the hardenability constituent of this invention, other various additive agents can be added further if needed. As these additive agents, for example A sensitizer, an antioxidant, light stabilizer, A silane coupling agent, an antiaging agent, thermal polymerization inhibitor, a leveling agent, a surface-active agent, a spray for preventing static electricity, preservation stabilizer, colorant, an ultraviolet ray absorbent, a plasticizer, lubricant, inorganic system fillers other than the paints (G) ingredient of this invention, an organic system filler, a wettability improving agent, a painted-surface improving agent, etc. are mentioned.

[0095]As a sensitizer, triethylamine, diethylamine, N-methyldiethanolamine, Ethanolamine, 4-dimethylaminobenzoic acid, 4-dimethylamino methyl benzoate, There are 4-dimethylamino ethyl benzoate, 4-dimethylamino isoamyl benzoate, etc., and YUBEKURIRU P102, 103, 104 and 105 (above, product made by UCB), KAYACURE DMBI, EPA (above, Nippon Kayaku Co., Ltd. make), etc. are mentioned as a commercial item.

[0096]As an antioxidant, Irganox 1010, 1035, 1076, and 1222 (above, Ciba-Geigy make) etc. are mentioned. As an ultraviolet ray absorbent, it is Tinuvin P, and 234, 320, 326, 327, 328 and 213 (above). The Ciba-Geigy make, Sumisorb 110, 130, 140, 220, 250, 300, 320, 340, 350, and 400 (above, Sumitomo Chemical Co., Ltd. make), etc. are mentioned.

[0097] As light stabilizer, Tinuvin 292, 144, 622LD (above, Ciba-Geigy make), SANORU LS-770, 765, 292, 2626, 1114, 744 (above, made in Mitsui Chemical Industry), etc. are mentioned. As a silane coupling agent, gamma-aminopropyl triethoxysilane, As gamma-mercapto propyltrimethoxysilane, gamma-meta-acryloxyprophyltrimethoxysilane, and a commercial item, SH6062, SZ6030 (above, Toray Industries Dow Corning silicone company make), KBE903, KBM803 (above, product made from Shin-etsu Silicone), etc. are mentioned.

[0098]As an antiaging agent, Antigene W, S, P, 3C, 6C, RD-G, FR, AW (above, Sumitomo Chemical Co., Ltd. make), etc. are mentioned. As a spray for preventing static electricity, polyoxyethylene amines and polyoxyethylene alkylamide. Polyoxyethylene alkyl ether and polyoxyethylene alkyl phenyl ether. Non-ion system sprays for preventing static electricity, such as glycerine fatty acid esters and sorbitan fatty acid ester species, Anionic system sprays for preventing static electricity, such as alkyl sulfonate, alkyl benzene sulfonate, alkyl sulfate, and alkyl phosphate, quarternary ammonium salt, an alkyl betaine, etc. are mentioned.

[0099]To the hardenability constituent of this invention, an epoxy resin, an acrylic resin, The polymer of an acrylic group content monomer and N-vinyl pyrrolidone, urethane acrylate, Polymerization nature compounds, such as vinyl ether, propenyl ether, and a maleic acid derivative, Polyamide, polyimide, polyamidoimide, polyurethane, polybutadiene, Chloroprene, polyether, polyester, a pentadiene derivative, Styrene / butadiene / styrene block copolymer, styrene / ethylene / butene / styrene block copolymer, Styrene / isoprene / styrene / block copolymer, the acrylic group content resin that uses styrene as a main chain ingredient, Polymer, such as petroleum resin, xylene resin, ketone resin, fluorine system oligomer, silicone series oligomer, and polysulfide system oligomer, or oligomer can also be blended suitably.

[0100]In polyisocyanate compound (I) this invention, fluoride oligomer (B) and a polyisocyanate compound can be blended and a hardenability constituent can also be obtained. As such a polyisocyanate compound, 2, 4-toluene diisocyanate, 2,6-toluene diisocyanate, Isophorone diisocyanate, hexamethylene di-

isocyanate, diphenylmethylene diisocyanate, (o, m, or p)-xylenediisocyanate, methylenebis (cyclohexylisocyanate), At least one kind chosen from trimethyl hexamethylene di-isocyanate, cyclohexane-1,3-dimethylene diisocyanate, cyclohexane-1,4-dimethylene diisocyanate, and 1,5-naphthalene diisocyanate is mentioned.

[0101] In the hardenability constituent which consists of fluorination oligomer (B) and a polyisocyanate compound, the polymeric polyol or the dihydroxy compound used by generation of usual polyurethane can be used together. As polymeric polyol, specifically A polyethylene glycol, At least one kind of polyether system diol chosen from a polypropylene glycol and a polytetramethylene glycol, At least one kind of polyester system diol chosen from ester of polyhydric alcohol and polybasic acid, At least one kind of poly lactone system diol chosen from at least one kind of polycarbonate system diol, polycaprolactone diol, and polybutyrolactonediol which are chosen from hexamethylene carbonate and pentamethylene carbonate is mentioned. One kind or two or more kinds may be combined out of these polyether system diol, polyester system diol, polycarbonate system diol, and poly lactone system diol.

[0102]Although the number average molecular weights of such polymeric polyol are 200-2000, they are 600-1500 still more preferably. The polymer which stiffened urethane and unsaturation ORGANO oligomer which especially used the thing of the molecular weight 850 by the polytetramethylene glycol, In 269% of ductility, the intensity of 382 kg / $cm^2$, and polycaprolactone diol. If the thing of the molecular weight 1000 is used, similarly by polycaprolactone diol, 314% of ductility, the intensity of 293 kg / $cm^2$, and the outstanding characteristic of [ if the thing of the molecular weight 1250 is similarly used ] 383% of ductility, and the intensity of 417 kg / $cm^2$ will be obtained.

[0103]It is preferred that it is at least one kind specifically chosen from the glycol which has a hydrocarbon skeleton of the carbon numbers 2-10 as a dihydroKISHIRU compound. It is desirable to use the glycol of the carbon numbers 2-6 still more preferably. Specifically as such a glycol, ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, etc. are mentioned.

[0104][0104]. Such polymeric polyol or dihydro one, a RU compound is 10 preferably to 100 weight % of hardenability constituents.

It is quantity % and is 30 to 50 weight % more preferably.

A polyisocyanate compound is 10 to 50 weight % preferably to 100 weight % of hardenability constituents. 15 to 30weight % of quantity is used more preferably.

[0105]In preparation of the hardenability constituent of preparation this invention of the hardening constituent which consists of fluoride oligomer (A), Although an order which mixes each ingredient is not essential, the inorganic particle which are an ease of work and a paints (G) ingredient makes it usually distribute, and from an easy viewpoint. Reactive diluent, such as fluoride oligomer (A) and an acrylic monomer (meta) (C), It is preferred to stir until it blends paints (G) and an inorganic particle distributes uniformly to the mixture in which other hardening agents (F) etc. were added a polymerization initiator (D) or a radical generator (E), the organic solvent as other additives (H), and if needed. The viscosity of the obtained hardening constituent is usually 5 - 50,000 mPa-s preferably one to 100,000 mPa-s in 25 **.

[0106]The coat of the hardenability constituent of this invention can be carried out on a base material by various methods by which normal use is carried out. As such a coating method, methods, such as dip

coating, a spray coat, a flow coat, a roll coat, and screen-stencil, can be mentioned, for example. The thickness of the coat in these coating is usually 0.1-50 micrometers.
It is 1-10 micrometers preferably.

[0107]In order to stiffen the hardenability constituent which has fluorination oligomer (A) of this invention, an electron beam, ultraviolet rays, an activity energy line, and heat can be used. Among these, when making it harden by light, it is preferred to use ultraviolet rays. as ultraviolet rays to be used, the wavelength of 400 nm or less can be included and a metal halide lamp and a mercury-vapor lamp (high voltage, a medium voltage, and low pressure -- any may be sufficient.) can be used as a light source, for example. As irradiation light quantity, it is usually 0.01 - 10J/$cm^2$, and is 0.1 - 3J/$cm^2$ more preferably.
[0108]When the constituent of this invention contains a solvent, after coating a constituent, preferably for 1 second - 24 hours within the limits of 10 seconds - 1 hour, Preferably, after drying a volatile constituent if needed at the temperature of 40-100 ** still more preferably, radiation irradiation can be carried out and 20-150 ** of 0-200 ** can also be hardened.
The hardenability constituent which consists of preparation main chain both-ends alcoholic hydroxyl group content fluoride oligomer (B) of the hardening constituent which consists of fluoride oligomer (B), and polyisocyanate compound (I) can perform a condensation reaction by the usual method, and can be stiffened. To this hardenability constituent, the additive agent (H) of polymeric polyol or a dihydroKISHIRU compound, other hardening agents (F), paints (G), and others can be added suitably if needed.
[0109][0109]. ** and the sex constituent concerning the use and directions-for-use this invention of a hardening constituent are ********s.
It excels and uses for a paint, sealant, a liquefied casting gasket, printing ink, adhesives, etc.
When painting a hardenability constituent directly as a paint, spray painting and the roll coat method are used preferably. When using the hardenability constituent concerning this invention for printing ink, offset, photogravure offset, and a flexo system are used preferably. When using a liquefied dispenser, it is also possible to form a sealant between seal things or on a sealing surface by sealant restoration and In Place Gasket (IPG), and since hyperviscosity and high thixotropy are required in this case, a thickness of 50micro - 10 mm is required.
[0110]
[Effect of the Invention]By making a hardenability constituent contain the fluoride oligomer which contains a functional group in the both ends of the main chain concerning this invention, a cure rate is quick and the hardenability constituent excellent in tough nature, elasticity, elasticity, etc. can be provided.
[0111]
[Working example]Although an working example explains this invention below, this invention is not limited at all by these working examples.
[0112]
[Work example 1][Main chain both-ends methyl ester group content fluoride oligomer] 156 g of main chain both-ends carboxyl group content fluoride oligomer and the methanol 1017g which were obtained by the method indicated by Tokuganhei10-150743 were introduced into the separable flask with a content volume of 3 l. After this fluoride oligomer dissolved thoroughly, $H_2SO_4$6.2g is dropped, and the outside temperature

of the flask was warmed to 100 **, and was refluxed for 3 hours. 75 to 80% of methanol was distilled off after flowing back, after neglecting the solution containing a reactant until it became a room temperature, it introduced slowly into 10-times the amount water, agitating water, and the sediment was obtained with the decanter. After rinsing a sediment about 5 times, it was made to dry for two days in 50 ** decompression oven, and the consistency yellow compound 149g was obtained. Yield was 95.5%. About the obtained consistency yellow compound, it identified by IR and NMR and checked that this compound was fluoride oligomer of a vinylidene fluoride system which has methyl ester in the both ends of a main chain.

[0113]IR spectrum: 1781 $cm^{-1}$(-$COOCH_3$) [-COOH is 1771 $cm^{-1}$].

$^1$H-NMR(acetone, TMS):3.909ppm (- $COOCH_3$)

[0114]

[Work example 2][Main chain both-ends unsaturation group content fluoride oligomer] 131 g and THF586g were introduced into the separable flask with a content volume of 1 l. for the main chain both-ends methyl ester group content fluoride oligomer obtained in working example 1. After this fluoride oligomer dissolved thoroughly, the flask was cooled all over the water bath into which ice was put, and the outside temperature of the flask was maintained at about 0-5 **. Then, 7.8 g of allylamine was dropped into the flask, and it was made to react for 1 hour. Output was transferred to the eggplant flask after ending reaction, and THF was distilled off by the evaporator. The acquired resultant was dried in 40 ** decompression oven as it is overnight, and the consistency reddish brown [ transparent ] compound 128.6g was obtained. Yield was 98.2%. About the obtained compound, it identified by IR and checked that this compound was fluoride oligomer of a vinylidene fluoride system which has an allyl group [-($CONHCH_2CH=CH_2$)$_2$] in the both ends of a main chain.

IR spectrum: 3462 $cm^{-1}$, 1543 $cm^{-1}$ (CO-NH)

1717 $cm^{-1}$ (N-H)

1654 $cm^{-1}$ ($CH=CH_2$)

[0115]

[Work example 3][Main chain both-ends alcoholic hydroxyl group content fluoride oligomer] in the working example 2, except having used 130 g of methanol amine instead of allylamine, Like the working example 2, when main chain both-ends methyl ester group content fluoride oligomer was amidated, the consistency reddish brown [ transparent ] compound 126.9g was obtained. Yield was 97.6%. About the obtained compound, it identified by IR and NMR and checked that this compound was fluoride oligomer of a vinylidene fluoride system which has an alcoholic hydroxyl group [-($CONHCH_2CH_2OH$)$_2$] in the both ends of a main chain.

IR spectrum: 1711 $cm^{-1}$ (-CONH-)

$^1$H-NMR(acetone, TMS):3.6-3.8ppm (-$CH_2OH$)

[0116]

[Work example 4][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] to output 50phr of the working example 2. omega-carboxy polycaprolactone

monoacrylate (ARONIX M-5300 (made by Toagosei)) 25phr and light ester CH(product made from Kyoeisha Chemistry)25phr were added and stirred, and the transparent yellow mixture was obtained. When the constituent as for which 0.03phr Kuwae **** obtained the photopolymerization initiator (IRGACURE 819 (product made from Tiba Chemistry)) into this mixture was irradiated with UV of 500W for 13 minutes, the hardened material which was excellent in elongation in the brown of optical transparence was obtained.

[0117]

[Work example 5][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] Methoxy triethylene glycol acrylate 25phr and ARONIX M-5300 (made by Toagosei) 25phr were added and stirred to output 50phr of the working example 2, and the transparent yellow mixture was obtained. When this mixture was irradiated with the photopolymerization initiator (IRGACURE 819 (product made from Tiba Chemistry)) and 0.03phrs, in addition the obtained constituent were irradiated with UV for 15 minutes, the hardened material excellent in beige elongation was obtained.

[0118]

[Work example 6][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] 50phrs were added to output 50phr of the working example 2, the light ester CH (product made from Kyoeisha Chemistry) was stirred to it, and the transparent yellow mixture was obtained. When this mixture was irradiated with the photopolymerization initiator (IRGACURE 819 (product made from Tiba Chemistry)) and 0.03phrs, in addition the obtained constituent were irradiated with UV for 15 minutes, the beige and tough hardened material was obtained.

[0119]

[Work example 7][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] MTG-A(product made from Kyoeisha Chemistry) 25phr and light ester CH (product made from Kyoeisha Chemistry)25phr were added and stirred to output 50phr of the working example 2, and the transparent yellow mixture was obtained. When the constituent which added and obtained photopolymerization initiator 0.1phr which mixed IRGACURE 819 and IRGACURE 1700 (product made from Tiba Chemistry) at a rate of 1:1 into this mixture was irradiated with UV for 15 minutes, the hardened material which was excellent in elasticity in translucent yellow was obtained.

[0120]

[Work example 8][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] Light ester CH(product made from Kyoeisha Chemistry)50phr was added and stirred to output 50phr of the working example 2, and the transparent yellow mixture was obtained. When the constituent which added and obtained photopolymerization initiator 0.11phr which mixed IRGACURE 819 and IRGACURE 1700 (product made from Tiba Chemistry) at a rate of 1:1 into this mixture was irradiated with UV for 20 minutes, case hardening was good, and the glossy tough hardened material was obtained.

[0121]

[Work example 9][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] to output 30phr of the working example 2. To the constituent which added MTG-A(product made from Kyoeisha Chemistry) 70phr, and stirred and obtained it. Vanadium (III) acetylacetonate (V(III)-AAc) 0.3phr, trimethyl phosphate (TMP) 3.6phr, and 1, 4-benzoquinone (PBQ)

0.25phr were added and stirred, and the brown mixture was obtained. When polymerization initiator cumene hydroperoxide (CHPO, Nippon Oil & Fats Co., Ltd. make) 4.6phr was added to this mixture and it was made to harden at ordinary temperature, the translucent yellow hardened material which was excellent in elasticity was obtained.

[0122]

[Work example 10][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] to output 50phr of the working example 2. V(III)-AAc 0.32phr and TMP3.1phr could be added to the constituent which added ARONIX M-5300 (made by Toagosei) 50phr, and stirred and obtained it, it stirred, and the transparent yellow mixture was obtained. When polymerization initiator CHPO (made by Nippon Oil & Fats Co., Ltd.) 4.7phr was added to this mixture and it was stiffened at ordinary temperature, the hardened material of the beige color excellent in elongation was obtained.

[0123]

[Work example 11][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] to output 50phr of the working example 2. MTG-A(product made from Kyoeisha Chemistry) 33phr, and ARONIXM-5300 V(III)-AAc 0.3phr, TMP 3.33phr, and PBQ0.17phr were added to the constituent which added 17phr, and stirred and obtained it, it stirred well, and the brown mixture was obtained. When polymerization initiator CHPO (made by Nippon Oil & Fats Co., Ltd.) 4.57phr was added to this mixture and it was stiffened at ordinary temperature, the hardened material with the good gloss of case hardening was obtained.

[0124]

[Work example 12][Hardening constituent which consists of main chain both-ends unsaturation group content fluoride oligomer] to output 50phr of the working example 2. MTG-A 25phr and ARONIX M-5300 V (III)-AAc 0.28phr, TMP 2.9phr, and PBQ 0.3phr could be added to the constituent which added 25phr, and stirred and obtained it, respectively, it stirred, and the brown mixture was obtained. When polymerization initiator CHPO (made by Nippon Oil & Fats Co., Ltd.) 4.26phr was added to this mixture and it was made to harden at ordinary temperature, the good brown hardened material of elasticity and elongation was obtained.

[0125]

[Work example 13][Hardening constituent which consists of main chain both-ends alcoholic hydroxyl group content fluoride oligomer] Acetone is added to the output 4.3g of the working example 3, It was considered as the 50% constituent of fluoride oligomer, and the 3,3'-dimethyl- 4 and 0.91 g of 4'-biphenylene di-isocyanate were added and stirred there, and the consistency brown mixture was obtained. The obtained mixture was heated for 15 minutes in 120 more ** oven in 40 ** oven for 10 minutes, and the ocherous tough hardened material was obtained.

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[Translation done.]